



GB04/4186



INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport

South Wales
NP10 8QQ

18 OCT 2004

WIPO

PCT

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Stephen Hordley

Dated 6 October 2004

BEST AVAILABLE COPY

THE PATENT OFFICE
A
25 OCT 2003

The Patent Office

2706703-EB7366-1 D02944
P01/7700.0.00-0324947.1

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference	SMC 60622/GB/P1		
2. Patent application number (The Patent Office will fill in this part)	0324947 1		25 OCT 2003
3. Full name, address and postcode of the or of each applicant (underline all surnames)	Avecia Limited Hexagon House Blackley Manchester, M9 8ZS United Kingdom Patents ADP number (if you know it) 07764137001 ✓ If the applicant is a corporate body, give the country/state of its incorporation GB		
4. Title of the invention	PROCESS		
5. Name of your agent (if you have one)	FAWKES, David Melville John Magall Avecia Limited Hexagon House Blackley Manchester, M9 8ZS United Kingdom Patents ADP number (if you know it) 2480511002		
6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of filing (day / month / year)
7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application		Date of filing (day / month / year)
8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d))			

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.
Do not count copies of the same document

Continuation sheets of this form

Description

Claim(s)

Abstract

Drawing(s)

18

03

CF

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

1

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

G. Shepherd

Date 23/10/03.

Avecia Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Mrs K.M. Pinder/Mrs G. Shepherd 0161 721 1361/2

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.

This form is a copy of the original and must be kept for at least 10 years.

APPLICANTS

AVECIA LIMITED

TITLE

PROCESS

PROCESS

The present invention relates to a process for etching metals and alloys which comprises applying to the surface of the metal or alloy an etch-resist ink by an ink jet printer, solidifying the ink without the use of actinic and / or particle beam radiation, chemically removing the exposed metal or alloy by a chemical etching process and optionally removing the etch-resist ink.

Photochemical machining (PCM) of metals and alloys is an alternative process to mechanical etching (e.g. drilling, stamping, cutting and related processes) of metal/alloy surfaces for the manufacture of decorative and industrial articles. Etching may be restricted to the surface as in the case of artistic articles and jewellery or it may involve total penetration as in the case of industrial articles. The metal/alloy may be in the form of a sheet, foil or an article and when in the form of a thin sheet or foil, the metal/alloy may be physically supported by a non-etchable substrate which may be optionally removed in the final etched article.

Traditional PCM is a complex process involving the prior preparation of a photo-tool.

Firstly, a metal or alloy surface is coated with an etch-resist layer. A photo-tool is prepared which is a negative of the required etch image and is often a silver photographic emulsion plate. The photo-tool is placed directly over the etch-resist layer and is then exposed to UV light. This causes the etch-resist layer to polymerise and harden in those areas exposed to the UV light to produce a latent negative image of the required etch in the etch-resist layer. The etch-resist layer is then chemically treated to remove the unexposed and unpolymerised area of the etch-resist. This is known as the development step. This chemical treatment is typically mildly alkaline where the etch-resist layer contains free acid groups.

The exposed metal or alloy is then selectively removed by chemical etching from those areas not protected by the etch-resist layers. Finally, the etch-resist is optionally removed. This is typically achieved by treatment with alkaline media for example using stronger aqueous alkali where the etch-resist contains free acid groups.

Although the process is widely used in the manufacture of etched metals and alloys it is tedious, expensive and wasteful of materials since the etch-resist layer is made separately and applied over the total area of the metal or alloy substrate. Furthermore, the photo-tool containing the negative image of the desired etch pattern is often distanced from the etch-resist layer so that diffraction of the UV light irradiation occurs leading to development and polymerisation in unwanted areas of the etch-resist directly beneath the photo-tool masked areas. This needs to be taken into consideration when preparing the photo-tool and can reduce the density and definition of etched features of finer detail.

Therefore, there exists a significant attraction in applying an etch-resist to specific areas of a metal or alloy surface using ink jet printing technology since it removes the

need for a photo-tool. The image, or negative image, is made digitally available direct from a computer, the number of processing steps is halved, the frequent need for differential stripping of the photo-resist using different strengths of aqueous alkali is avoided and since there is no photo-tool which is distanced from the photo-resist layer there is the potential for improved definition and density of any fine detail. There also exists the cost saving in terms of etch-resist material since the etch-resist is only applied to those areas to be protected from chemical etching.

Actinic or particle beam radiation curing etch-resist inks have some disadvantages, in particular long term storage requires dark conditions, curing can be difficult for very thick layers or for etch-resist inks containing highly opaque pigments and curing requires significant energy input.

EP0746 638 discloses solvent based or hot melt inks for ink jet printed etch resist inks used in the manufacture of textured rollers. However EP0746 638 discloses nothing regarding the composition of such inks, how adhesion of the etch-resist ink to the metal or alloy surface might be improved or how the etch-resist might be removed.

The chemical composition of the etch-resist ink needs to be very carefully controlled since it must adhere to the metal or alloy surface during the etching step and must be made readily removable if desired. Typically the removal is carried out by chemical treatment after etching. A preferred etch-resist removal method utilises alkali. The fine details in PCM etching can be seriously compromised if either the unexposed etch-resist is incompletely removed or if some of the exposed and polymerised etch-resist is removed prior to chemically etching the metal or alloy. The requirements for adhesion and removability pose a difficult balance in etch-resist ink chemistry.

There is therefore an attraction in providing non-actinic or particle beam radiation curing etch-resist inks suitable for ink jet which show good adhesion to the metal or alloy surface during etching and which can be optionally removed from the metal or alloy surface.

Certain inks have been found to be effective as metal or alloy etch-resist inks which can be applied by ink jet. A feature of all these inks is that they are liquid when fired from the ink jet printer nozzle but can readily be solidified in flight and/or once on the surface of the metal or alloy. Solidification can be by any means known in the art other than actinic light and / or particle beam radiation. Preferred examples of solidification methods include cooling (e.g. phase change or hot melt inks), heating (e.g. thermal cure and cross-linking or reactive inks) and liquid evaporation (e.g. both aqueous and organic solvent inks where a resin is used). Further by incorporation of metal chelating groups into the carrier vehicle of the etch-resist the adhesion during etching can be much improved.

According to the invention there is provided a process for etching a metal or alloy surface which comprises applying an etch-resist ink by ink jet printing to selected areas of the metal or alloy, solidifying the etch-resist ink without the use of actinic light and / or

particle beam radiation and then removing the exposed metal or alloy by a chemical etching process wherein the etch-resist ink comprises the components:

- A) 60 to 100 parts carrier vehicle comprising one or more components which contain at least one metal chelating group;
- 5 B) 0 to 40 parts colorant; and
- C) 0 to 5 parts surfactant;

wherein the ink has a viscosity of not greater than 30 cPs (mPa.s) at the firing temperature, all parts are by weight and the total number of parts A)+B)+C) = 100.

The metal or alloy may be supported by a non-etchable substrate. If present the non-etchable substrate is preferably removed after etching.

THE CARRIER VEHICLE

The carrier vehicle which is component A) provides fluidity to the etch-resist ink during firing and application to the metal or alloy surface. The carrier need not be liquid at 25°C but must be liquid at the firing temperature. The firing temperature is typically from 10°C to 200°C, but is more preferably from 10°C to 150°C.

The carrier vehicle is also functionally that component which facilitates solidification of the etch-resist ink as a whole. The preferred embodiments of such carrier vehicles are hot melt, thermal cure and volatile etch-resist inks. Thus in the case of a hot melt etch-resist ink the carrier is a wax or polyamide resin or mixture thereof which solidifies on cooling. In the case of thermal cure etch-resist inks the carrier contains one or more thermally reactive monomers, prepolymers or mixtures thereof which solidify on heating. In the case of volatile etch-resist inks the carrier comprises a volatile liquid and a resin wherein the volatile liquid is evaporated from the etch-resist ink, typically by heating, leaving a solidified resin-bound etch-resist ink.

Because of trends in legislation regarding volatile organic liquids and the desirability of minimising odour during the printing process it is preferably the etch-resist ink is essentially free from any volatile organic liquid.

By essentially free it is meant that only trace or residual levels of volatile organic liquids are lost through evaporation. Preferably not more than 1% and more preferably not more than 0.1% by weight of volatile organic liquid relative to the total amount of etch-resist ink is evaporated from the metal or alloy surface after printing. Such volatile organic liquids are herein defined as those having a boiling point below 200°C. Typical examples include low molecular weight alcohols, ketones, esters, ethers and amides.

The hot melt and thermal cure embodiments of the present invention are preferred over the volatile etch-resist ink embodiment.

VOLATILE ETCH-RESIST INKS

In the case of volatile etch-resist inks the carrier vehicle comprises a volatile liquid (which is liquid at 25°C and has a boiling point of less than 200°C) and a resin. After the volatile etch-resist ink is printed the volatile liquid is evaporated from the metal or alloy surface leaving behind the etch-resist ink bound by the resin. The volatile liquid can be

evaporated by heat and/or reduced pressure but it is preferable that the volatile liquid has a boiling point of less than 175°C, more preferably less than 150°C and especially less than 110°C at 1 atmosphere of pressure.

The volatile liquid may be a polar liquid or a non-polar liquid or a mixture thereof. By the term "polar" in relation to the volatile liquid it is meant that a volatile liquid is capable of forming moderate to strong bonds as described in the article entitled "A Three Dimensional Approach to Solubility" by Crowley et al in Journal of Paint Technology, Vol. 38, 1966, at page 269. Such liquids generally have a hydrogen bonding number of 5 or more as defined in the abovementioned article.

Examples of suitable polar volatile liquid are amines, ethers, especially lower alkyl ethers, organic acids, esters, ketones, glycols, alcohols, amides, ureas, sulphoxides, sulphones and especially water. Numerous specific examples of such moderately strongly hydrogen bonding liquids are given in the book entitled "Compatibility and Solubility" by Ibert Mellan (published in 1968 by Noyes Development Corporation) in Table 2.14 on pages 39-40 and these liquids all fall within the scope of the term polar volatile liquid as used herein.

Preferred polar volatile liquids are dialkyl ketones, alkyl esters of alkane carboxylic acids and alkanols, especially such liquids containing up to, and including, a total of 6 carbon atoms. As examples of the preferred and especially preferred liquids there may be mentioned dialkyl and cycloalkyl ketones, such as acetone, methyl ethyl ketone, diethyl ketone, di-isopropyl ketone, methyl isobutyl ketone, di-isobutyl ketone, methyl isoamyl ketone, methyl n-amyl ketone and cyclohexanone; alkyl esters such as methyl acetate, ethyl acetate, isopropyl acetate, butyl acetate, ethyl formate, methyl propionate, methoxy propylacetate and ethyl butyrate; glycols and glycol esters and ethers, such as ethylene glycol, 2-ethoxyethanol, 3-methoxypropylpropanol, 3-ethoxypropylpropanol, 2-butoxyethyl acetate, 3-methoxypropyl acetate, 3-ethoxypropyl acetate and 2-ethoxyethyl acetate; alkanols such as methanol, ethanol, n-propanol, isopropanol, n-butanol and isobutanol and dialkyl and cyclic ethers such as diethyl ether and tetrahydrofuran. Especially preferred solvents are alkanols, alkane carboxylic acids and esters of alkane carboxylic acids.

Preferred non-polar volatile liquids are non-halogenated aromatic hydrocarbons (e.g. toluene and xylene), halogenated aromatic hydrocarbons (e.g. chlorobenzene, dichlorobenzene, chlorotoluene), non-halogenated aliphatic hydrocarbons (e.g. linear and branched aliphatic hydrocarbons containing six or more carbon atoms both fully and partially saturated), halogenated aliphatic hydrocarbons (e.g. dichloromethane, carbon tetrachloride, chloroform, trichloroethane) and natural non-polar organics (e.g. vegetable oil, sunflower oil, linseed oil, terpenes and glycerides).

A preferred volatile liquid is water.

When water is the volatile liquid it may be used in combination with a water-immiscible organic solvent but more preferably it is used with a water-miscible organic solvent.

Suitable water-immiscible organic solvents include aromatic hydrocarbons, e.g. toluene, xylene, naphthalene, tetrahydronaphthalene and methyl naphthalene; chlorinated aromatic hydrocarbons, e.g. chlorobenzene, fluorobenzene, chloronaphthalene and bromonaphthalene; esters, e.g. butyl acetate, ethyl acetate, methyl benzoate, ethyl benzoate, benzyl benzoate, butyl benzoate, phenylethyl acetate, butyl lactate, benzyl lactate, diethyleneglycol dipropionate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di (2-ethylhexyl) phthalate; alcohols having six or more carbon atoms, e.g. hexanol, octanol, benzyl alcohol, phenyl ethanol, phenoxy ethanol, phenoxy propanol and phenoxy butanol; ethers having at least 5 carbon atoms, preferably C₅₋₁₄ ethers, e.g. anisole and phenetole; nitrocellulose, cellulose ether, cellulose acetate; low odour petroleum distillates; turpentine; white spirits; naphtha; isopropylbiphenyl; terpene; vegetable oil; mineral oil; essential oil; and natural oil; and mixtures of any two or more thereof. Benzyl alcohol is especially preferred.

Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the carrier vehicle comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Preferrably the volatile etch-resist ink comprises water and water-miscible organic solvent in the ratio from 99:1 to 50:50, more preferably from 95:5 to 60:40.

The resin component in the volatile etch-resist ink may be a natural or synthetic resin. Preferred natural resins include saccharides (especially starch, xanthan, guar), proteins (especially casein and whey) and natural waxes.

Preferred synthetic resins include polyethylenics (especially polyvinyl polymers), polyethers, polyamides, polyesters and polycarbonates. Preferred polyvinyl polymers include poly(meth) acrylates, poly styrenics, polyethylene and polypropylene.

The resin may be a homopolymer, a copolymer or a blend of two or more resins.

The number average molecular weight of the resin is preferably greater than 5,000 and especially between 5,000 and 5,000,000.

The resin may be present in the etch-resist ink in the form of a solution, dispersion or mixture thereof. For resins which are present in the volatile etch-resist ink as a dispersion (rather than a solution) the volume average particle size is preferably less than 1 micron, more preferably less than 0.5 of a micron in order to inhibit the blocking of the ink jet printer nozzle.

Preferably the resin is capable of forming a continuous film on evaporation of the volatile liquid. This may require heating from 50 to 150°C but it is preferred that the resin is capable of forming a film at approximately 25°C.

More than 20% by weight of resin in the carrier vehicle tends to give rise to higher viscosities and ink jet firing problems. Thus preferred volatile etch-resist inks have a carrier vehicle which comprises from 1 to 20 percent, more preferably from 3 to 15 percent and especially from 3 to 10 percent by weight of resin relative to the total amount of carrier vehicle.

A preferred firing temperature for volatile etch-resist inks is from 10 to 80°C, more preferably a temperature from 10 to 35°C and especially from 20 to 25°C.

HOT MELT INKS

In the case of hot melt inks the carrier vehicle is a material which is solid at 25°C but which is liquid and can be ink jet fired at a suitable firing temperature. The firing temperature is typically in the range 50 to 200°C, but is preferably from 50 to 150°C and especially from 70 to 120°C. Preferred hot melt ink carriers melt at a temperature from 40 to 120°C. For such inks the viscosity is preferably not greater than 30cPs at 120°C. Hot melt inks and compositions are described more fully in US 6336720. Preferably the carrier vehicle is a wax or polyamide resin or mixtures thereof. Suitable Polyamide resins include Tohmides™ (manufactured by Fujikasei), Polymides™ (manufactured by Sannyoukasie) and Versamid™ manufactured by Henkel. Suitable waxes include petroleum wax, polyethylene wax, plant wax, animal wax, ketone wax, polyester wax, higher alcohol wax and the like. Preferably the hot melt ink has a sharp transition between solid and liquid phase as the temperature is raised and hence crystalline or semi-crystalline carrier vehicles are preferable.

THERMAL CURE INKS

In the case of thermal cure inks the carrier vehicle is a material which is liquid at 25°C and can be fired from an ink jet printer. The ink droplets can then be thermally cured in flight and/or on the metal or alloy to solidify the etch-resist ink. A preferred thermal cure temperature is from 50 to 175°C, more preferably from 50 to 150°C and especially 80 to 150°C. The carrier vehicle contains at least one thermally reactive liquid monomer or more preferably a mixture of two or more thermally reactive liquid monomers.

The term monomer is used to include traditional monomers, macromonomers and prepolymers. The thermal cure is achieved by the incorporation of thermally reactive cross-linking groups into one or more components of the carrier vehicle which cause cross-linking on heating. Preferred cross-linking groups are epoxy, amine, imine, activated olefinic bonds, N-alkylol, silane, aziridine, keto, aldehyde, acetoacetoxy, phenolic, melamine, formaldehyde, hydroxy, carboxy, and carbodiimide.

Preferably all of the thermally reactive liquid monomers in the carrier vehicle are capable of cross-linking with at least two other monomer molecules. The cross-linking may be via hydrogen bonding or ionic bonding but is preferably co-valent in nature.

A catalyst may be optionally incorporated into the etch-resist ink to accelerate the thermal cure and solidification. However it is preferable that the catalyst be added to the etch-resist ink immediately prior to the time of use to inhibit premature reaction and poor ink jet firing.

One embodiment of thermal cure reactive inks is a one pack composition. Here the thermal cure ink comprises all the final ink components such that it solidifies on the substrate when heated. Preferably the cross-linking groups in a one pack approach are blocked as described in US 6341856. This helps prevent pre-reaction of the etch-resist ink.

When more than one type of thermally reactive liquid monomer is used the cross-linking groups on at least one monomer are preferably chosen to be co-reactive with the groups on at least one other thermally reactive liquid monomer (e.g. epoxy with amine). The preferred pairings of thermally reactive cross-linking groups are as indicated across the rows of Table 1.

TABLE 1

Thermally reactive cross-linking group	Thermally Co-reactive cross-linking group
Epoxy	Amine, anhydride, thiol, acid, hydrazine, phenolic, N-alkyl.
Hydroxy / thiol	Isocyanates, epoxy, anhydride, acid, N-alkyl, carbodiimide, aziridine.
Anhydride	Epoxy, amine, hydroxy, isocyanate, aziridine, carbodiimide, thiol.
Acid	Epoxy, amine, hydroxy, isocyanate, aziridine, carbodiimide, N-alkyl.
Cyclic carbonate, aldehyde, keto, activated olefinic bond, N-alkyl, acid, anhydride, acid chloride, acetoacetoxy.	Amine
Activated olefinic bond	Amine, thiol, radical initiator, cationic initiator, dienes (Diels-alder reactive).
Amine / Hydrazine	Epoxy, isocyanate, aldehyde, diketester, activated olefinic bond, N-alkyl.
Silane, halosilane, alkoxy silane, acetosilane, silicate, silanol	Hydroxy, acid, isocyanate, silane, halosilane, alkoxy silane, acetosilane, silicate, silanol.
Imine	Aldehyde, epoxy, anhydride, isocyanate, ester, acetoacetoxy, activated olefinic bond.
Metal salts and complexes	Carboxy, keto, aldehyde, acetoacetoxy, phosphonic acid, imine, amino and thio.
Formaldehyde	Melamine, urea, phenol, resorcinol.

In embodiments where the thermally reactive liquid monomer contains an activated olefinic group a preferred means of cross-linking and solidification is by the additional incorporation of a thermal radical initiator into the carrier vehicle.

Suitable thermal radical initiators include peroxides, azos and persulphates. Preferred examples of thermal initiators include persulphates especially sodium and ammonium persulphate (APS), peroxides especially benzoyl peroxide (BPO), t-butyl hydroperoxide (tBHPO) and lauryl peroxide (LPO), and azos, especially azobisisobutyronitrile (AIBN).

These may be used with synergists such as organic amines. Preferred thermal radical initiators are those which are stable at 25°C but can be activated by heating to a temperature less than 150°C.

Preferred activated olefinic groups are (meth)acrylates and especially acrylates.

With mixtures of thermally reactive liquid monomers it is advantageous to separate all the thermally reactive liquid monomers with similar cross-linking groups of one type from all of the other (e.g. separating all the amines from all the epoxys) until immediately prior to use. Such separation helps to inhibit premature reaction which can result in nozzle blockage or poor printer firing.

It is even more preferable to have some of the curing components (catalyst and/or thermally reactive liquid monomer) of the etch-resist ink absent from the ink during firing but which are incorporated into the ink on the metal or alloy surface. For example a

catalyst might be previously applied to an alloy surface on which the etch-resist ink will be printed. Alternatively an amine containing thermally curing liquid monomer might be post added onto the surface of a metal or alloy to which an epoxy containing etch-resist ink has already been applied. Such combination schemes are described in US 4,694,302, US 5,380,769, US 5,645,888 and US 5,853,861. It is preferred for such embodiments that both curing components are applied by ink jet printing especially wherein the ink jet printer comprises at least two cartridges and at least two printing heads such that each curing component may be stored and fired separately.

Thus a second embodiment of the thermal cure reactive ink is a two pack system. Here part of the thermally reactive liquid monomer and/or part of the catalyst is omitted from the etch-resist ink during firing but is subsequently combined to give the full etch-resist ink composition on the metal or alloy surface. This approach is particularly useful for very reactive etch-resist inks which would cure prior to ink jet firing if used as a one pack composition.

Preferably at least one of the thermally reactive liquid monomers has a number average molecular weight of less than 10,000.

In order to increase the rate of thermal solidification it is often advantageous to have at least one thermally reactive monomer or polymer present in the carrier vehicle which has on average not less than 3 and especially not less than 10 cross-linking groups per molecule. Such monomers and polymers often have higher molecular weights and thus tend to raise the ink viscosity. Hence such monomers and polymers are preferably used at not more than 10% by weight on the total etch-resist ink. Examples of polymers which have on average not less than 3 cross-linking groups per molecule include for example polyols, polyisocyanates, polyepoxys, polyamines and polyimines, poly(meth)acrylates and poly siloxanes. Examples of monomers which have on average not less than 3 cross-linking groups per molecule include for example tri, tetra, penta and hexa functional isocyanates, alcohols, amines, epoxys, (meth)acrylates, siloxanes and imines.

Preferably the thermal cure ink is fired at a temperature of less than 100°C, more preferably less than 80°C, especially less than 50°C and most especially at approximately 25°C. Thus a preferred ink for thermally curing etch-resist inks has a viscosity of less than 30cPs at 25°C. A preferred method for ink jet firing is using a piezo ink jet printer rather than a thermal ink jet printer. Preferably piezo firing is carried out at approximately 25°C.

PREFERRED ETCH-RESIST AND CARRIER VEHICLE INK EMBODIMENTS

Although the above carrier vehicle embodiments are preferred it will be readily appreciated by those skilled in the art that a multitude of approaches within the present invention exist where aspects of one carrier vehicle embodiment are combined with those of another. Thus by example it is possible to use a thermally curable etch-resist ink which contains some volatile liquid. Similarly a hot melt etch-resist ink can comprise thermal reactive liquid monomers.

METAL CHELATING GROUPS

The metal chelating group may be any group which can form a bond with the metal or alloy and especially with ferrous metals and alloys. The surface of the metal or alloy may optionally be prepared prior to applying the etch-resist ink. This preparation can be effected by atmospheric exposure or can be the result of a chemical or physical treatment process. Atmospheric exposure often results in the formation of oxides (e.g. iron, aluminium, zinc), hydrated oxides (e.g. $\text{Fe}_3\text{O}_4 \cdot x\text{H}_2\text{O}$) and carbonates (e.g. copper). Examples of chemical surface treatments are acid etching (e.g. HCl , HNO_3 , H_2SO_4 , H_3PO_4) and oxidizer etching (e.g. persulphates and perborates). Examples of physical treatments are heating, plasma exposure and irradiation. The metal chelating group or groups are capable of binding with the surface of the metal or alloy without any preparation although adhesion is often improved following such pretreatments.

The metal chelating group is any moiety which contains a hydrogen atom capable of being displaced by the metal of the metal or alloy surface or which possesses a lone pair of electrons capable of forming a bond with said metal. Examples of such groups are hydroxides, especially aryl or heteroaryl hydroxides such as phenolic hydroxides; amines which may be aliphatic, aryl or heteroaryl; mercaptans which may be aliphatic, aryl or heteroaryl; carboxylic acids which may be aliphatic, aryl or heteroaryl; oximes and ketoximines; acetaryl amides; hydroxy silanes and silicones; N-containing heterocycles such as imidazoles, benzimidazoles, triazoles, benzotriazoles, thiazoles, isothiazoles, acid anhydrides, and acid groups (especially carboxylic acid groups, phosphoric acid groups, polyphosphoric acid groups, and sulphonic acid groups). Where more than one type of metal chelating group is used the metal chelating groups may be the same or different. In one preferred class of metal chelating groups which contains two chelating groups, the chelating groups are attached to adjacent carbon atoms such as β -diketones, β -keto esters, β -keto aldehydes and β -keto heterocycles.

Less preferred metal chelating groups are hydroxides, amines which may be aliphatic, aryl or heteroaryl; or mercaptans which may be aliphatic, aryl or heteroaryl.

More preferred metal chelating groups are ketoximines; acetaryl amides; hydroxy silanes and alkoxy silanes; aryl or heteroaryl hydroxides (such as phenolic hydroxides); N-containing heterocycles (preferably imidazoles, benzimidazoles, triazoles, benzotriazoles, thiazoles, isothiazoles); acid anhydrides; β -diketones, β -keto esters, β -keto aldehydes, β -keto heterocycles; and acid groups (particularly carboxylic acids groups, phosphoric acid groups, polyphosphoric acid groups and sulphonic acid groups). Especially preferred metal chelant groups are β -diketones, β -keto esters, β -keto aldehydes and β -keto heterocycles.

An especially preferred metal chelating group is a carboxylic acid group.

One or more components of the carrier vehicle must contain at least one metal chelating group. Said component can be the wax or polyamide resin (as in the case of hot melt etch-resist inks), the resin (as in the case of volatile etch-resist inks) or the thermally

reactive liquid monomer (as in the case of thermal cure etch-resist inks). These are preferred embodiments as the metal chelating groups is then chemically bound into the solidified etch-resist ink. Less preferably the component containing at least one metal chelating group can be a low molecular weight compound (having a molecular weight less than 1,000) which is not chemically bound into the final solidified etch-resist ink.

For hot melt inks it is preferred that the carrier vehicle is a wax or polyamide resin or mixtures thereof. Preferably the metal chelating group or groups are incorporated by selecting a wax or polyamide resin having at least one metal chelating group. Especially preferred are waxes and polyamide resins having at least one carboxylic acid group as the metal chelating group. Preferred waxes containing at least one carboxylic acid group include oxidized waxes, polyester waxes and long chain fatty acids. Suitable long chain fatty acids include long chain aliphatic carboxylates such as palmitates, stearates, laurates and the like.

For thermal cure inks the metal chelating group or groups are preferably incorporated in a thermally reactive liquid monomer. For thermally cured inks comprising an activated olefinic group the metal chelating group or groups are preferably incorporated in an activated olefinic monomer.

For volatile etch-resist inks the metal chelating group or groups are preferably incorporated in the resin. Especially preferred resins are poly (meth)acrylics, polyurethanes and polyester comprising at least one metal chelating group. Alternatively resins comprising at least one metal chelating group can be readily prepared by the polymerisation of monomers wherein at least one of the monomers contains one or more metal chelating groups.

Preferably the resin comprises at least one acidic group and more preferably at least one carboxylic acid group. In the case of synthetic resins such carboxylic acid group or groups are preferably incorporated by means of a carboxylic acid containing monomer. Preferred carboxylic acid containing monomers for making polyolefins are acrylic acid, itaconic acid, beta carboxy ethyl acrylate, maleic acid and especially methacrylic acid. A preferred carboxylic acid monomer for making polyurethanes is dimethylol propanoic acid. Carboxy terminated polyesters are readily made by using a stoichiometric excess of the acid. Many natural resins exist which contain carboxylic acid such as carboxy celluloses, proteins containing glutamic acid and natural or oxidized waxes.

It is preferred that the weight of the metal chelating group or groups in the etch-resist ink is not less than 0.1, more especially not less than 0.25 and especially not less than 0.4 parts by weight relative to the total weight of the etch-resist ink. Preferably the weight of metal chelating group or groups in the etch-resist ink is not greater than 30 parts, more preferably not greater than 20 parts and especially not greater than 10 parts by weight relative to the total weight of the etch-resist ink. Preferred carriers comprise from 0.1 to 30, more preferably from 0.25 to 20 and especially 0.4 to 10 parts by weight of metal chelating group or groups relative to the total weight of the etch-resist ink.

ACID GROUPS IN THE CARRIER VEHICLE

As hereinbefore described acid groups and especially carboxylic acid groups are the preferred metal chelating groups. Such groups exhibit good adhesion properties with ferro metals and alloys. Acid chelating groups also aid the optional removal of the etch-resist after the etching step. A particularly preferred means of removing the etch-resist when the etch-resist ink contains at least one acid group is by treatment with alkaline media and especially treatment with alkaline aqueous media.

The acid group or groups in the component in the carrier vehicle may be in the salt form but are preferably in the free acid form. Preferred salts forms include metal salts such as sodium, potassium, lithium as well as ammonium, substituted ammonium, quaternary ammonium, pyridinium and benzalkonium salts. Such salts are preferably not strongly chelating with the acid functional group.

It is preferred that at least one component in the carrier contains at least one acid metal chelating group and the etch-resist ink has an acid value of greater than 30, more preferably greater than 40mg KOH/gm. Although inks having an acid value above 150 mg KOH/g may be used, there is generally no advantage in such levels. In fact high acid levels can result in premature removal of the etch-resist ink during the etching step. Thus it is preferred that at least one component in the carrier contains at least one acid metal chelating group and the etch-resist ink has an acid value from 40 to 150mg KOH/g.

In some embodiments where adhesion and alkali removability need to be independently controlled it is preferable to have two or more types of metal chelating group present wherein at least one of the metal chelating groups is an acid group and at least one of the metal chelating groups is not an acid group. This may be in different carrier components but it is preferable that such groups are incorporated into the same carrier component.

THE COLORANT

The colorant which is component B) of the etch-resist ink, when present, is preferably a pigment and may be organic or inorganic including those pigments with surface modification which facilitates self dispersion in the ink. The pigment may be from any of the recognised classes of pigments described, for example, in the Third Edition of the Colour Index (1971) and subsequent revisions of and supplements thereto under the chapter headed "Pigments". Examples of inorganic pigments are titanium dioxide, Prussian blue, cadmium sulphide, iron oxides, vermillion, ultramarine and the chrome pigments, including chromates, molybdates and mixed chromates and sulphates of lead, zinc, barium, calcium and mixtures and modifications thereof which are commercially available as greenish-yellow to red pigments under the names primrose, lemon, middle, orange, scarlet and red chromes. Examples of organic pigments are those from the azo, diazo, condensed azo, thioindigo, indanthrone, isoindanthrone, anthanthrone, anthraquinone, isodibenzanthrone, triphenyldioxazine, quinacridone and phthalocyanine series, especially copperphthalocyanine and its nuclear halogenated derivatives, and also

lakes of acid, basic and mordent dyes. Carbon black, although strictly inorganic, behaves more like an organic pigment in its dispersing properties. Preferred organic pigments are phthalocyanines, especially copper phthalocyanines, monoazos, diazos, indanthrones, anthanthrones, quinacridones and carbon blacks.

5 A preferred colour for the etch-resist ink is blue.

The pigment is typically incorporated into the etch-resist ink jet ink composition by milling it together with one or more components of the carrier vehicle and in the presence of a dispersant. The dispersant is preferably a polyester/polyamine and is, for example, a dispersant as disclosed in US 6,197,877. Dispersants of this type are available under the trademark Solsperse™ dispersants (Avecia Ltd). The dispersant may also include a dispersant synergist (also known as a fluidizer) such as a quaternary ammonium salt of a partially sulphonated copper phthalocyanine pigment. Examples of such dispersant synergists are disclosed in GB-A-1508576, GB-A-2108143 and WO 01/14479 and are available under the Solsperse™ trademark.

15 The ratio of dispersant to dispersant synergist is typically from 1:1 to 10:1 by weight and is preferably about 5:1 by weight. The total amount of dispersant and dispersant synergist to pigment may vary over wide limits and is typically from 50% to 150% by weight relative to the weight of colorant. The amount of colorant in the etch-resistant ink is preferably not greater than 4 parts, more preferably not greater than 3 parts and especially not greater than 2 parts by weight.

20 SURFACTANT

The surfactant which is component C) of the etch-resist ink composition, when present, may be any surface-active material which aids the homogeneity of the ink and/or provides desirable surface tension and wetting properties to the resultant ink. The surfactant may also be selected to adjust the firing characteristics of the ink composition within the desired limits. The surfactant is preferably anionic and especially non-ionic and is preferably aliphatic in nature, optionally containing silicon atoms and/or fluorine.

25 Surfactants in inks often bloom to the surface of the solidified ink and cause a mottled or matte appearance. This surfactant bloom may also result in reduced resistance of the etch-resist ink to the conditions of metal or alloy etching. Thus it is preferred that the surfactant contains at least one reactive group that can be chemically bonded within the solidified etch-resist ink. This bonding may be hydrogen bonding but is preferably a salt bond and especially a covalent bond.

30 The etch-resist ink preferably has a surface tension of from 20 to 40 and especially between 25 and 35 mN/m. Consequently, the amount of component C) is generally from 0.0 to 0.6 parts.

OTHER ETCH-RESIST INK ADJUVANTS

40 The etch-resistant ink may contain other adjuvants which are commonly used in ink jet printing ink compositions in addition to components A) to C) specified above. Such adjuvants include slip modifiers, thixotropic agents, foaming agents, anti-foaming agents,

waxes, oils, plasticisers, binders, antioxidants, photo-initiator stabilisers, gloss agents, fungicides, bactericides, organic and/or inorganic filler particles, levelling agents, opacifiers and antistatic agents.

PREFERENCES FOR ETCH-RESIST INKS

5 Preferred etch-resist inks are filtered through a filter having a pore size of 10 microns, more preferably 5 microns and especially 1 micron to remove particles which might block an ink jet nozzle.

Preferably the viscosity of the etch-resist ink is from 8 to 15 cPs (mPa.s) at the firing temperature.

10 METAL OR ALLOY

The metal or alloy can be any of those suitable for Photochemical Machining (PCM) and includes metals and their alloys from group IA, group IIA, group IIIB, group IVB, group VB, group VIB, the transition metals, the lanthanides and actinides of the Periodic Table according to Mendeleef, as published for example on the front inside cover
15 of *BASIC INORGANIC CHEMISTRY*, COTTON/WILKINSON/GAUS, second Ed, ISBN 0-471-85151-5.

Suitable metals and alloys include aluminium, bronze, beryllium, chromium, columbium, constantan, copper and copper alloys, gold, nickel and nickel alloys, lead, magnesium, molybdenum, niobium, platinum, silver, stainless steel, mild steel, tin,
20 titanium, tungsten, vanadium, zinc and zirconium. Preferred metals and alloys are stainless steel, mild steel, beryllium, beryllium copper, copper, Inconel, Kovar, Monel and other nickel alloys especially Ferro nickel alloys such as Invar and alloy 42; nickel, aluminium, brass, molybdenum and titanium. Ferro metals and alloys are especially preferred.

25 Prior to applying the etch-resist ink to the metal or alloy, the metal surface is preferably cleaned by any method known to the art which includes rinsing in organic solvent, rinsing with aqueous detergent solution, mechanical abrasion such as sand-blasting, micro-etching with aqueous acids (e.g. HCl and H₂SO₄) and aqueous oxidative cleaning with, for example, persulphate or perborate.

30 PRINTING PROCESS

The etch-resist ink may be applied to the metal or alloy surface using any of the ink jet printing processes known in the art. Printing can be performed by a thermal ink jet printer or an electrostatic ink jet printer but preferably the printer is a piezo ink jet printer. Printing can be carried out either continuously or by a drop on demand (DOD) process.
35 The thickness of the ink jet printed etch-resist can be varied widely according to the specific requirements of the metal or alloy and etchant used. Preferably the etch-resist is from 1 to 50 microns thick. In some applications it is advantageous to vary the thickness of the etch-resist over the metal or alloy surface. This can facilitate greater versatility and control in the etch step. In the case of hot melt inks the etch-resist ink is heated prior to
40 and curing firing to melt and liquify the ink.

SOLIDIFICATION STEP

The solidification step may be performed by any means known in the art other than by exposure of the etch-resist ink to actinic light and / or particle beam radiation sources. Preferably solidification is achieved by cooling, heating or by evaporation of at least one volatile liquid component of the carrier vehicle. Other less preferred methods of solidification include exposure to air (so called alkyd curing resins), exposure to moisture (applicable to cyano acrylates for example) and electrolytic coagulation. For hot melt inks (also known as phase change inks) the method of solidification is cooling. A hot melt ink is fired in its molten state and on cooling to an ambient temperature below 30°C (typically 25°C to 15°C) the etch-resist ink solidifies (freezes). The metal or alloy surface can be cooled below 25°C if faster solidification is needed. In the case of thermally cured etch-resist inks the solidification is achieved by heating. Heating can be performed by any means known in the art but the use of hot air, the application of heat underneath the metal or alloy (i.e. to a non-printed surface) and the use of infra-red or microwave radiation are particularly suitable. In the case of the volatile etch-resist inks the method of solidification is by evaporation of a volatile liquid in the etch-resist ink which leaves the etch-resist ink bound by resin. The volatile liquid may evaporate readily at 25°C or heating may be used to facilitate or speed evaporation. Evaporation of the volatile liquid may also be accelerated by a reduction in pressure though this is less preferable to heating.

ETCHING STEP

After solidification of the etch-resist ink the metal or alloy is subjected to a chemical etching process to remove those parts of the metal or alloy which are not protected by the solidified etch-resist ink. The removal of this metal or alloy results in the desired etch pattern. The etching may be restricted to the surface or may fully penetrate the metal or alloy.

The chemical etching may be carried out by any means appropriate to the metal or alloy concerned. Table 2 summarises the preferred etchants for preferred metals and alloys.

TABLE 2

Metal	Common etchants*	Temperature °C
Stainless steel (many grades)	35-42 °Bé FeCl ₃	35-55
Mild steel	35-42 °Bé FeCl ₃	35-55
Beryllium copper	30-42 °Bé FeCl ₃ or ammoniacal copper or 33 °Bé acidic CuCl ₂	40-55
Copper and copper alloys	30-42 °Bé FeCl ₃ or ammoniacal copper or 33 °Bé acidic CuCl ₂	40-55
Inconel and other high nickel alloys	38-42 °Bé FeCl ₃ or conc nitric/conc hydrochloric acid/water 1:1:3	45-55
Aluminium	20% Na OH or conc hydrochloric acid/water 1:4 or alkaline potassium ferricyanide	60-90 20-65 55
Brass	30-42 °Bé FeCl ₃ or ammoniacal copper or 33 °Bé acidic CuCl ₂	40-55
Molybdenum	Alkaline potassium ferricyanide or 40 °Bé Fe(NO ₃) ₃	55 40-55
Titanium	10-50% HF (optionally with HNO ₃)	30-50

* The concentration of etchant (column 2) is measured in Degrees Baume (°Bé)

where:

°Bé = 145 (SG – 1/SG); and

SG is the specific gravity (density) of the solution.

Etching is typically carried out at a temperature from 20 to 100°C although it is preferably between 25 and 60°C and includes spraying or dipping where the metal or alloy may be contacted with the chemical etchant when in either the horizontal or vertical position.

Spraying is preferred, especially where the metal or alloy is in the vertical position since this allows for quicker removal of the chemical etchant containing removed metal and/or alloy. The speed of etching may be accelerated by agitating the chemical etchant, for example, using sonic agitation.

POST ETCH TREATMENT

After the metal or alloy has been treated with the chemical etchant it is preferably rinsed with an organic solvent or more preferably with water to remove traces of the etchant.

OPTIONAL REMOVAL OF THE ETCH-RESIST INK

The solidified etch-resist ink may be left in place on the surface of the metal or alloy. Thus according to a further aspect of the present invention there is provided a metal or alloy partially coated with a solidified etch-resist ink.

Alternatively the solidified etch-resist ink may be removed after etching. Preferably removal is achieved by chemical treatment and more preferably removal is by treatment with alkaline media where the etch-resist contains one or more acid groups. Alkaline removal is especially effective with etch-resist inks which contain one or more acid metal chelating groups. The alkaline media can be solvent based but is preferably aqueous. Solvent based alkaline media preferably contain organic amines, especially alkanolamines such as ethanolamine in an organic solvent. Preferred organic solvents are polar in nature as these tend to wet metals and alloys better and since the polar solvent itself may readily be washed from the metal with water. However, it is much preferred to use aqueous alkaline media, typically containing alkalis such as ammonia, metal hydroxides, carbonates and bicarbonates.

Typically alkaline treatment is performed at a temperature from 0 to 100°C, preferably 40 to 60°C to remove the etch-resist ink.

Alternative less preferred methods for removing the etch-resist ink include solvent stripping, heating, abrasion, ultrasound, burning/oxidizing, cutting and plasma treating. Solvent stripping can be performed in non-polar aprotic solvents (e.g. aromatic solvents and halogenated solvents) or in polar aprotic solvents (e.g. Dimethyl sulphoxide, dimethyl formamide, N-methyl pyrrolidone etc).

Thus according to a further aspect of the present invention there is provided a metal or alloy wherein the solidified etch-resist ink has been removed after etching.

NON-ETCHABLE SUPPORT

In embodiments where a non-etchable support has been used, said support is preferably removed at some point after etching. The non-etchable support is preferably a non-metallic material, more preferably a ceramic, glass, wood, textile, wax, paper, plastics material or rubber material.

PREFERRED ARTICLES

According to a further aspect of the present invention there is provided an article having a chemically etched surface pattern or design and especially an article where the etchant fully penetrates the metal or alloy creating holes. Examples of specific articles are a grid, a filter, a graticule, a mesh, a light chopper disc, a heat sink plate, a heater element, a screen, colour TV mask, a diaphragm, a shim, a gasket, a washer, a spring, a cog, a link, a probe, a magnetic recording head, a circuit lead frame, an encoder disc, an

item of jewellery, a rule, a scale, a clutch plate, an emitter contact, a micro reactor, a suspension lead, an ink jet nozzle plate, a stencil, a razor foil, a bearing, an edge filter, a logo, a nameplate, a decorative plaque, an instrument case, a box, an enclosure and a potentiometer case made by the process of the present invention.

CLAIMS

1. A process for etching a metal or alloy surface which comprises applying an etch-resist ink by ink jet printing to selected areas of the metal or alloy, solidifying the etch-resist ink without the use of actinic light and / or particle beam radiation and then removing the exposed metal or alloy by a chemical etching process wherein the etch-resist ink comprises the components:

A) 60 to 100 parts carrier vehicle comprising one or more components which contain at least one metal chelating group;

B) 0 to 40 parts colorant; and

C) 0 to 5 parts surfactant;

wherein the ink has a viscosity of not greater than 30 cPs (mPa.s) at the firing temperature, all parts are by weight and the total number of parts A)+B)+C) = 100.

2. A process as claimed in claim 1 wherein the metal chelating group(s) are selected from the group consisting of ketoximines; acetaryl amides; hydroxy silanes and alkoxy silanes; aryl or heteroaryl hydroxides; N-containing heterocycles; acid anhydrides; β -diketones, β -keto esters, β -keto aldehydes, β -keto heterocycles; and acid groups:

3. A process as claimed in claim 1 wherein the metal chelating group(s) are selected from the group consisting of imidazoles, benzimidazoles, triazoles, benztriazoles, thiazoles and isothiazoles.

4. A process as claimed in claim 1 wherein the metal chelating group(s) are selected from the group consisting of β -diketones, β -keto esters, β -keto aldehydes and β -keto heterocycles.

5. A process as claimed in claim 1 wherein the metal chelating group(s) are acid groups.

6. A process as claimed in claim 5 wherein the metal chelating group(s) are selected from the group consisting of carboxylic acid groups, phosphoric acid groups, polyphosphoric acid groups and sulphonic acid groups.

7. A process as claimed in claim 5 wherein the metal chelating group(s) are carboxylic acid groups.

8. A process as claimed in claim 1 wherein the carrier vehicle comprises two or more types of metal chelating groups wherein at least one of the metal chelating groups is an acid group and at least one of the metal chelating groups is not an acid group.

9. A process as claimed in any one of claims 1 to 8 wherein the etch-resist ink is solidified by cooling.

10. A process as claimed in any one of claims 1 to 9 wherein the etch-resist ink is essentially free from any volatile organic liquid.

11. A process as claimed in any one of claims 1 to 10 wherein the colorant is a pigment.

12. A process as claimed in any one of claims 1 to 11 wherein the colorant is blue.

13. A process as claimed in any one of claims 1 to 12 wherein the etch-resist ink has been filtered through a filter having a pore size of 1 micron.

14. A process as claimed in any one of claims 1 to 13 wherein the etch-resist ink has a surface tension of from 20 to 40 mN/m.

15. A process as claimed in any one of claims 1 to 14 wherein the viscosity of the ink is from 8 to 15 cPs (mPa.s) at the firing temperature.

16. A process as claimed in any one of claims 1 to 15 wherein the firing temperature is from 10 to 150°C.

17. A process as claimed in claim 1 wherein at least one component of the carrier vehicle contains at least one acid metal chelating group and the etch-resist ink has an acid value from 40 to 150mg KOH/g.

18. A process as claimed in any one of claims 1 to 17 wherein the metal or alloy is a ferro metal or ferro alloy.

19. A process as claimed in claim 1 wherein the carrier vehicle comprises a volatile liquid and a resin.

20. A process as claimed in claim 19 wherein the volatile liquid is water.

21. A process as claimed in claim 1 wherein the carrier vehicle is a wax or polyamide resin or mixtures thereof.

22. A process as claimed in claim 1 wherein the carrier vehicle is at least one thermally reactive liquid monomer.

23. A process as claimed in claim 22 wherein the thermally reactive liquid monomer contains an activated olefinic group and the carrier vehicle additionally comprises a thermal radical initiator.

24. A process as claimed in any one of claims 1 to 23 wherein the solidified etch-resist is removed after etching.

25. A process as claimed in claim 24 wherein the solidified etch-resist is removed by treatment with an alkaline media.

26. ~~An etched metal or alloy partially coated with a solidified etch-resist made by the process as claimed in any one of claims 1 to 23~~

27. An etched metal or alloy made by the process as claimed in claim 24 or claim 25.

28. A grid, a filter, a graticule, a mesh, a light chopper disc, a heat sink plate, a heater element, a screen, colour TV mask, a diaphragm, a shim, a gasket, a washer, a spring, a link, a probe, a magnetic recording head, a circuit lead frame, an encoder disc, an item of jewellery, a rule, a scale, a clutch plate, an emitter contact, a micro reactor, a suspension lead, an ink jet nozzle plate, a stencil, a razor foil, a bearing, an edge filter, a logo, a nameplate, a decorative plaque, an instrument case, a box, an enclosure and a potentiometer case made by a process as claimed in any one of claims 1 to 23 or claims 24 or 25.

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record.

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.